J. Chem. & Cheml. Sci. Vol.4 (1), 43-49 (2014)

Synthesis, Characterization and Solution Studies of Nano sized $(CTA)_4[v^{IV}ThMo_{12}O_{42}]8H_2O$, $(CTA)_4[Ni^{IV}CeMo_{12}O_{42}]8H_2O$, $(CTA)_4[Mn^{IV}CeMo_{12}O_{42}]8H_2O$, $(CTA)_4[Ni^{IV}CuMo_{12}O_{42}]8H_2O$

A. AROKIA NEPOLEAN RAJ and T. JEYABALAN

Department of Chemistry,
Sacred Heart College, Tirupattur, Tamil Nadu, INDIA.

(Received on: January 10, 2014)

ABSTRACT

Micro emulsion method has been successfully employed to synthesise Polyoxometalate(POM) nano particles using CTAB as the cationic surfactant for producing reverse micelle suitable for the proposed title compounds. The synthesized nano poly oxometalates were characterised using Infrared spectroscopy, X-ray diffraction, and Scanning electron microsope techniques. The synthesized nano particles are employed for the activity against some microbes and found effective in many cases. The synthesized nano particle also are employed for their effect on textile effluent and found to be very good water softener and found good in phenolphthalein degradation

Keywords: Nano polyoxometalate, microemulsion, anti microbial, effluent treatment.

1. INTRODUCTION

Synthesis of polyoxometalate has attracted much attention as they are widely used in many fields like catalysis[1-6]. There have been several investigations on polyoxometalates for their application as sensors and photovoltaic applications[7]. Also some quantum of research work is being done in the area of degradation of Industrial dye which is one of the most important environmental issue[8]. Polyoxometalates are also tested against some of the microorganisms for their antimicrobial activity[9]. Some of the Polyoxometalates were also prepared in nano scale[10-15]. But very limited amount of work being carried out to synthesis nano polyoxometalate successfully. And very limited nano sized polyoxometalates are tried for new

applications. Hense this work will try to test the ability of polyoxometalates on degradation of dyes present in textile effluent.

2. EXPERIMENTAL

2.1 Materials

Ammonium molybdate, nickel sulphate, ammonium cupric sulphate, ammonium ceric sulphate, Manganese sulphate, vanadyl sulphate, Hydrogen peroxide, n-Hexane n-butanol and Cetyltrimethylammonium-bromide (CTAB) are purchased from E-Merk and are used without any further purification

2.2. Analytical and Physical methods

Molybdenum was estimated graviatrically as oxinates. Thorium and cerium were estimated gravimetrically as ThO_2 and CeO_2. Nickel was estimated gravimetrically as Ni-DMG comples. Vanadium, Manganese and Copper were estimated spectrophotometrically[16]. The amount of water content was found by Heating the sample at 120^oC, until constant weight was obtained. IR spectra were recorded on BRUKER-ALPHA IR spectrophotometer using pellets of the materials diluted KBr. X-ray diffraction measurements were performed on a PAN analytical system Diffractometer (model DY-1656) using 2.2 KW Copper anode ceramic X- ray tube as source. The SEM image is recorded in JEOL Model JSM - 6390LV equipped with EDS JEOL Model JED – 2300.

2.3 Preparation of microemulsion

The microemulsion system for the synthesis of nano polyoxomolybdates was prepared as follows: 2 ml of cold water is added to a mixture of 2 ml n-butanol and 9 ml of n- hexane. The mixture is stirred for 15 minutes and after the solution becomes clear 2g of CTAB is added and the stirring is continued. Using this microemulsion the synthesis was continued with the suitable reagents for the respective nano particle.

2.4 Preparation of the complexes

Complexes (II), (III) and (IV) were prepared by mixing a solution of ammonium ceric sulphate(0.2 mole dm^{-3}) or ammonium cupric sulphate (0.2 mole dm^{-3}) to a boiling solution of ammonium molybdate (0.25 mole dm^{-3}) with continuous stirring. To the resulting solution aqueous solution of nickel sulphate (0.2 mole dm^{-3}) or Manganese sulphate (0.2 mole dm^{-3}) containing oxidant was added with stirring. The resulting solution was filtered, cooled and saturated with ammonium nitrate to salt out the complex. The resultant product was collected by centrifugation washed with alcohol and hot water for several times to remove the organic residue if any. Complex (I) was prepared by adapting a similar procedure used for the preparation of Complexes (II), (III) and (IV). However, no oxidant was added and vanadyl sulphate was used in the place of manganese sulphate.

2.5 Effluent treatment experiments

The synthesized Nanopolyoxomolybdate have been tested for textile effluent treatment. The effluent from textile industry in Tirupur was collected and its various parameters like hardness, concentration of the dyes like phenolphthalein and methyl orange, alkalinity and pH were measured by

testing the sample in Cleanchem, Salem. The efficacy of the synthesized complex was tested by adding 1g of synthesized compound with 50 ml of effluent taken in a beaker and stirred well for 5 hours and again the impacts it produced on the various parameters of the effluent are measured.

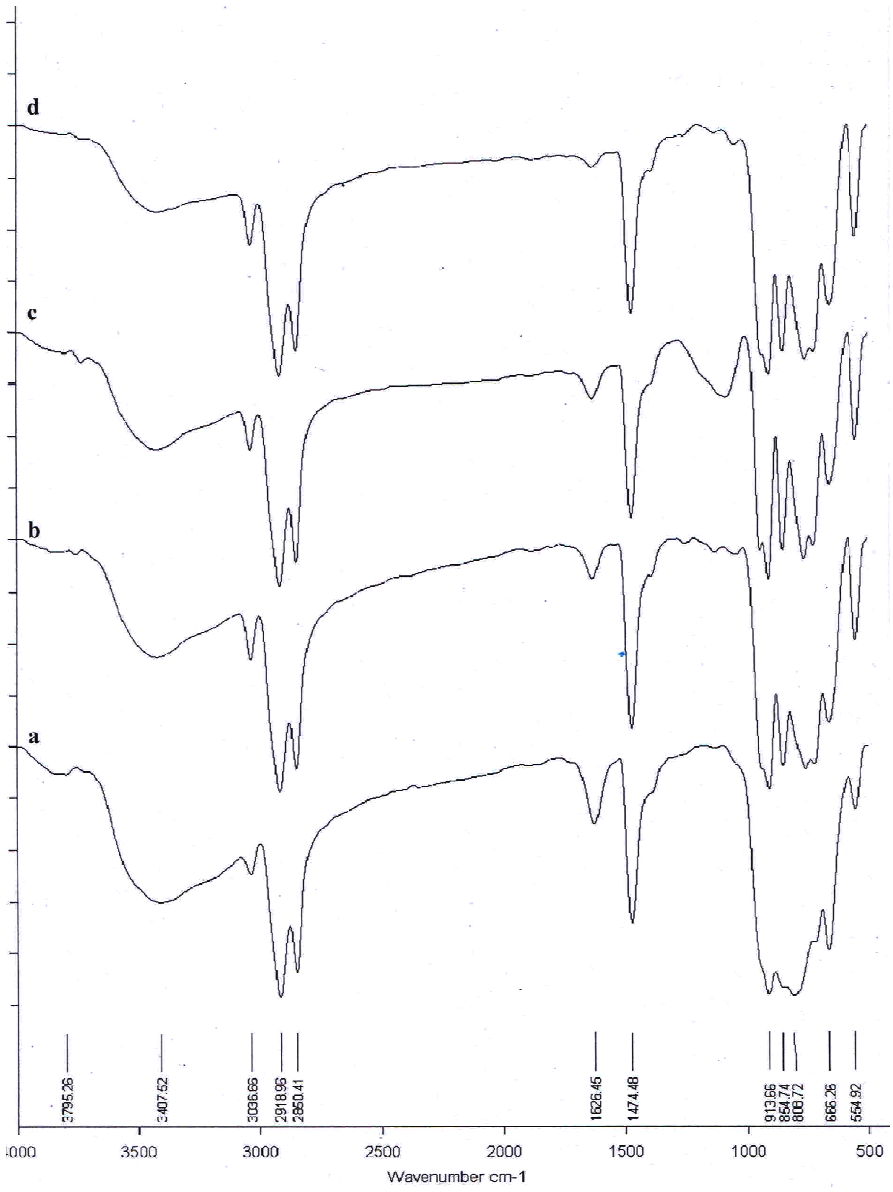

Figure 1: The IR spectrums of the complexes: a. $(CTA)_4[v^{IV}ThMo_{12}O_{42}]8H_2O$ b. $(CTA)_4[Ni^{IV}CeMo_{12}O_{42}]8H_2O$, c. $(CTA)_4[Mn^{IV}CeMo_{12}O_{42}]8H_2O$, d. $(CTA)_4[Ni^{IV}CuMo_{12}O_{42}]8H_2O$

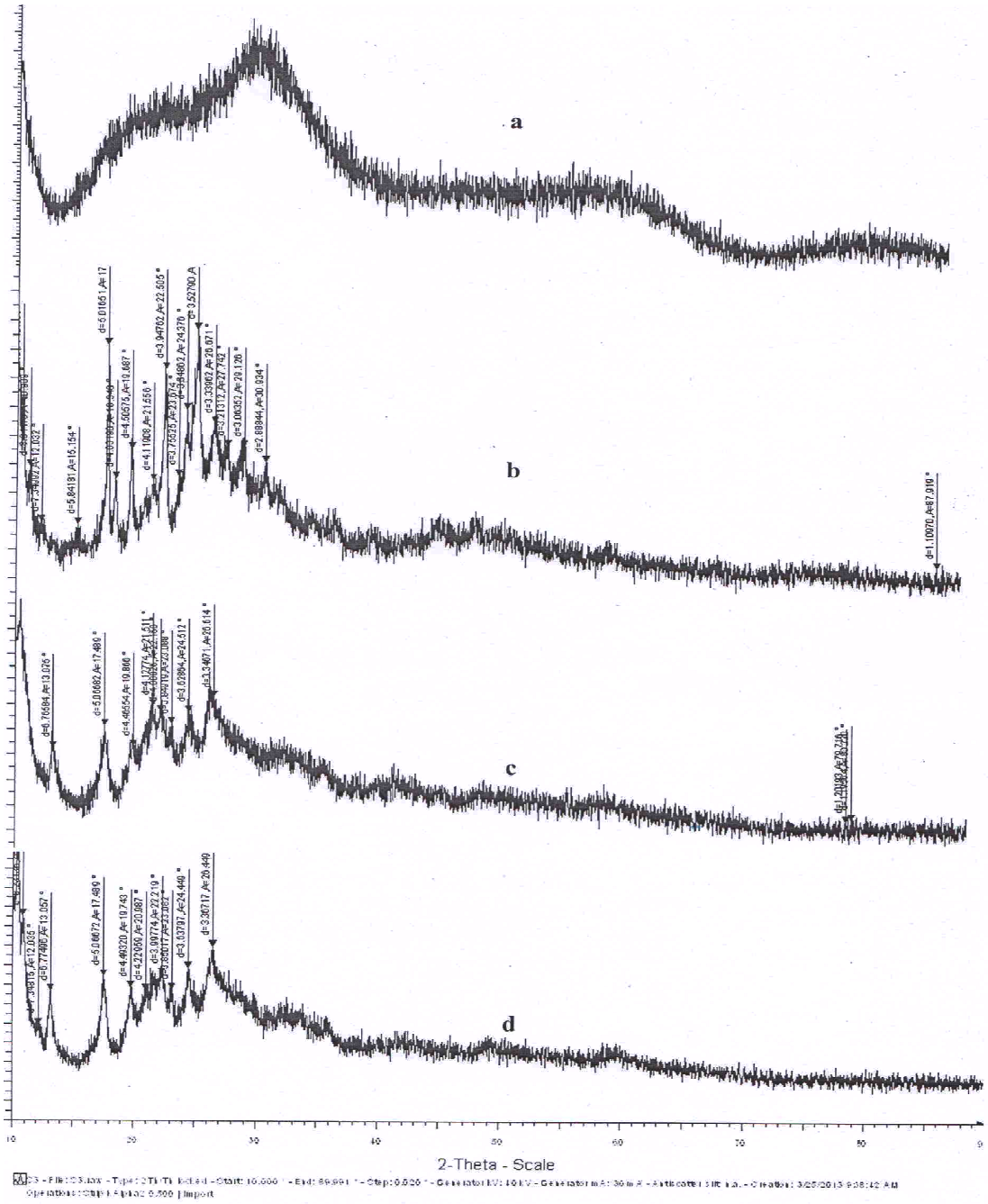

Figure 2. XRD pattern of the complexes a. $(CTA)_4[Ni^{IV}\ CuMo_{12}O_{42}]8H_2O$ b. $(CTA)_4[V^{IV}ThMo_{12}O_{12}]8H_2O$ c. $(CTA)_4[Ni^{IV}\ CeMo_{12}O_{42}]8H_2O$ d. $CTA)_4[Mn^{IV}\ CeMo_{12}O_{42}]8H_2O$

Table 1: IR Spectral data of the complexes

$(CTA)_4[v^{IV}ThMo_{12}O_{42}]8H_2O$ (I)	$(CTA)_4[Ni^{IV}CeMo_{12}O_{42}]$ $8H_2O$ (II)	$(CTA)_4[Mn^{IV}$ $CeMo_{12}O_{42}]$ $8H_2O$ (III)	$(CTA)_4[Ni^{IV}$ $CuMo_{12}O_{42}]8$ H_2O (IV)	Tentative assignments
913.66 cm^{-1}	911.59	912.67	912.87	ν_{Mo-Ot1}
854.74 cm^{-1}	853.49	854.33	855.09	ν_{Mo-Ot2}
765.36	766.35	762.91	764.06	ν_{Mo-Ob}
666.26 cm^{-1}	727.29 663.10	726.58 665.90	728.43 662.32	ν_{Mo-O-X} (X = Th, Ni, Mn)
2850.41 2918.96cm^{-1}	2850.78 2918.35	2850.59 2918.21	2850.90 2917.90	ν C-H

Table 2. Various Parameters of the effluent before and after adding the nano sized polyoxometalates

Complex	Parameters	Before adding the sample	After adding the sample
$(CTA)_4[V^{IV}ThMo_{12}O_{42}]8H_2O$	pH	9.2	8.3
	Phenalpthalin	150 ppm	10 ppm
	Metholorange	1950 ppm	1900 ppm
	Total Alkalinity	2100 ppm	1910 ppm
	Total Hardness	130 ppm	Nil
$(CTA)_4[Ni^{I}{}_{2}{}^{V}CeMo_{12}O_4]8\ H_2O$	pH	9.2	7.5
	Phenalpthalin	150 ppm	Nil
	Metholorange	1950 ppm	1900 ppm
	Total Alkalinity	2100 ppm	1900 ppm
	Total Hardness	130 ppm	Nil
$(CTA)_4[Mn^{I}{}_{2}{}^{V}CeMo_{12}O_{42}]8H_2O$	pH	9.2	7.5
	Phenalpthalin	150 ppm	Nil
	Metholorange	1950 ppm	1800 ppm
	Total Alkalinity	2100 ppm	1800 ppm
	Total Hardness	130 ppm	Nil
$(CTA)_4[Ni^{IV}CuMo_{12}O_{42}]$ $8H_2O$	pH	9.2	7.5
	Phenalpthalin	150 ppm	Nil
	Metholorange	1950 ppm	1900 ppm
	Total Alkalinity	2100 ppm	1900 ppm
	Total Hardness	130 ppm	Nil

3. RESULTS AND DISCUSSION

3.1 IR Studies

IR spectra of the complexes (I), (II), (III), and (IV) are given in figure 1. The structure of which has been well established[17]. The band frequencies and tentative assignments are given in table 1. IR spectroscopy is one of the promising technique to study the changes in the

structure of heteropolyanions[18]. The synthesized heteropolyanions give six featured peaks in the wave region of 550-1630 cm^{-1}. These peaks indicate the formation of Dexter type structure. The prepared nanomaterial exhibited the characteristic bands for organic CTAB. The stretching vibrations of C-H groups of CTA^{+} cations are observed at 2850-2918 cm^{-1}. The stretching vibrations observed at bands 3036 cm^{-1} and 3420 cm^{-1} were assigned for water molecules. These values can be seen in the IR spectra of the compound (figure 1).

3.2 XRD analysis

XRD patterns of the complexes (I), (II), (III), and (IV) are given in (figure 2).The particle size of the synthesized nano particles were analysed using Debye Scherrer equation ($D=K\lambda/\beta\cos\theta$), and found that the particles are in nanoscale around 20nm. It also evident that the size distribution of the nano particles are not uniform.

3.3 Effluent studies

The water analysis report of the complexes (I), (II), (III), and (IV) before and after adding the complexes are given in (table 2). The results show that there is significant decrease in the various parameters of the effluent sample. The pH of the effluent is reduced from 9.2 to 7.5 which is a good sign of effluent treatment since it is close to neutral. The phenolphthalein has been completely decomposed which shows that the compound has successfully degraded phenolphthalein and has little effect on the decomposition of methyl orange. On the alkalinity the compound had considerable effect by reducing it from 2100 ppm to 1800 ppm. The hardness of the water is completely vanished which is very good result as for as the effluent treatment is concerned. Therefore the compound served as very good water softner.

4. CONCLUSION

Four nano sized, polyoxomolybdates have been successfully synthesized in nano scale using micro emulsion method using CTAB as surfactant which was found suitable for nano polyoxometalates. The synthesized poyoxomolybdates were characterized by IR spectroscopy and the particles size was analysed by XRD using Shcerer formula. The nano size and morphology was examined by SEM images. The complexes were successfully employed in the treatment of effluent of the textile industry for the degradation of dyes like phenolphthalein, methyl orange and used as a water softner. The application of the compound in the textile effluent treatment is noteworthy. It can be witnessed from the changes it brought in the various parameters like changes in the pH, decomposition of the dyes like methyl orange and phenolpthalein. The hardness of the water completely went nil which explains that the compound can be used as a water softner. There also significant changes it produces in the total alkalinity.

Hence the compounds of this nature can be used as an efficient tool for the industrial effluent treatment which poses major threat in polluting the water. Since the area under research possesses various applications, the scope of it is vast so that further studies in this area of study will be fruitful for both science and to the society.

ACKNOWLEDGEMENT

We thank the Abraham Panampara Research Centre (APRC), Sacred Heart College, for Providing Research Facilities.

REFERENCES

1. Pope M T Heteropolyoxomanganates (Berlin, NewYork: Springer) 91, (1983).
2. Okuhara T, Hibi T and Misino M, *J. Chem. Soc., Chem Commun*, 697, 1984.
3. Hasik M, Pron A, Poznczek J, Beilanski A, Piwewarska Z, Kruczala K and Dziembaj R *J. Chem. Soc., Farady Trans*. 90 2099, (1994).
4. Dong S J, Wang G and Lin B F, Electrochim, *Act*a 40 1025, (1995).
5. Comuzzi C, Dolcetti G, Trovarelli A, Cavani F, Trifiro F, Llorca J and Finke R G, *Catal. Lett*. 36 75, (1996).
6. Pope M T, Zhang X Y, Oconnor C J and Jameson G B, Inorg. Chem. 35 30, 1996.
7. Ge Jin, Shi-Ming Wang, Wei-Lin Chen,* Chao Qin, Zhong-Min Su and En-Bo Wang*, *J. Mater. Chem. A*, 1, 6727, (2013).
8. Wang Yajun *et a*l, *Journal of Rare Earths*, 31, 360, (2013).
9. Kuo-Hui Wu *et al*., *Microporous and Mesoporous Materials* 118, 467, (2009).
10. Malika Ammam *J. Mater. Chem. A*, 1, 6291, (2013).
11. Laure Catalae and Louis Nadjo *J. Mater. Chem.*, 19, 8639, (2009).
12. Julian Eastoe , Martin J. Hollamby, *Laura Hudson Advances in Colloid and Interface Science* 128, 5, (2006).
13. Vuk Uskokovi´C∗ and Miha Drofenik, *Surface Review and Letters*, 12, 239, (2005).
14. Xian-Hua Zhang,a Su-Yuan Xie,*a Zhi-Yuan Jiang,a Li-Chuan Zhou,b Zhao-Xiong Xie,a Rong-Bin Huanga and Lan-Sun Zhenga, *Chem. Commun.*, 2032, (2002).
15. Yingwei Xie, Ruqiang Ye , Honglai Liu, Colloids and Surfaces A: *Physicochem. Eng. Aspects* 279, 175, (2006).
16. Vogel A I Text book of Inorganic quantitative analysis 4th edn (London: ELBS), (1978).
17. Kazansky L P, Malchanov V N, Tatjanina I V and Torchenkova E A *J. Chem. Soc., Chem.Commun*, 93, (1981).
18. Spitsyn V I, Kansky LP and Torchenkova E A, *Soc. Sci. Rev., Chem. Rev*. B3 111, (1981).